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Calculations of Second Moments of NQR Signals for Explosive Materials

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13. ABSTRACT (Maximum 200 words) Calculations of the second moments of Nuclear Quadrupole Resonance (NQR) signals are presented in this report. Numerical computations are performed for two explosive materials: cyclotrimethylene-trinitramine, RDX, and cyclotetramethylene, β -HMX. The report includes a discussion of vector and tensor analysis necessary for performing calculations in the nonorthonormal coordinate systems. The basic theory for calculations of second moments is described and the procedure for numerical computations is outlined. The listings of MATLAB® programs are also included. Calculations are performed for nuclei with spin $I = 1$ and asymmetric field gradient. For cases under consideration no external magnetic field is present. Calculations of the second moments include first order contributions due to dipolar interactions between completely equivalent nuclei and interactions between nuclei with the EFG tensors of the same magnitude but different orientation. The second order contributions from dipolar interactions between nitrogen and hydrogen nuclei are also considered.				
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CALCULATIONS OF SECOND MOMENTS OF NQR SIGNALS FOR EXPLOSIVE MATERIALS

1. INTRODUCTION

Over the last few decades numerous terrorist acts involving explosive materials have been executed. These present a real threat for society. The problem of security in planes, airports, postal service, and other ground installations has become such an important issue to lead the government to sponsor research on detection of explosive materials.

In recent years, the problem of explosives detection has been addressed by the research group at the Naval Research Laboratory. The work is sponsored by the Federal Aviation Administration and the Department of Defense, Office of Special Technologies. Techniques based on Nuclear Quadrupole Resonance (NQR) spectroscopy have been successfully developed for the detection of military type explosives, and narcotics. The research is aimed at the detection of small amounts of an explosive, possibly hidden in luggage or a postal package, where the properties of the explosive material, or its distribution, make X-ray methods fail.

In this report we present the calculations of the second moments of ^{14}N NQR signals for some military explosives. The calculations have been performed for RDX and β -HMX.

First we describe the crystal structures of the explosive materials. These structures were reported in the literature and obtained from X-ray and neutron-diffraction analysis. In the following two sections we discuss the basic concepts of the vector and tensor analysis in nonorthonormal systems, and outline of the procedure for the calculations of second moments. These two sections contain the formulae necessary for the numerical computations. A short introduction to the numerical calculations follows. Next, the results of the calculations of the second moments are presented and discussed. The last section summarizes the results of the work presented. Some mathematical derivations are given in the Appendices A and B. The Appendix C provides listing of the most important programs.

2. CRYSTAL STRUCTURE OF EXPLOSIVE MATERIALS

The well-known explosive compound, cyclotrimethylene-trinitramine, ($\text{C}_3\text{H}_6\text{N}_6\text{O}_6$), is commonly called RDX. It exists in two polymorphic forms, however, the crystal structure of only one form is known. The structure determination of the other form is impossible because of its extreme instability.

Another explosive compound, cyclotetramethylene tetranitramine, ($C_4H_8N_8O_8$), is known as HMX. It is a by-product of the manufacture of RDX. Four polymorphic forms of HMX exist, and of these β -HMX is stable at room temperature. Both compounds form rings of alternate CH_2 and $N-NO_2$ groups.

2. CRYSTAL STRUCTURE OF RDX

The crystal structure of RDX has been determined by X-ray diffraction methods. Subsequently, it was refined from single-crystal neutron-diffraction data^{1,2}. The unit cell is orthorhombic and space group is $Pbca$, Figure 1. The unit cell parameters are: $a = 13.182(2)$, $b = 11.574(2)$, $c = 10.709(2)\text{\AA}$. There are eight molecules per unit cell. Carbon atoms have tetrahedral symmetry, the $N-NO_2$ groups are planar. The molecule of RDX has a plane of nearly mirror symmetry. The plane is defined by atoms C2, N1, and N4.

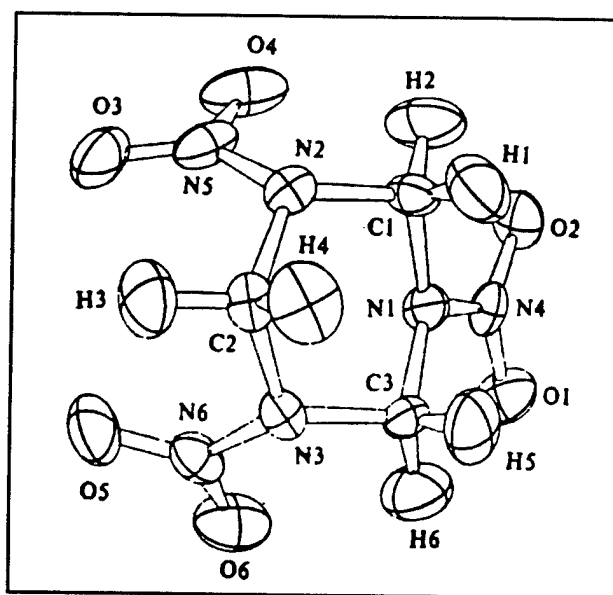


Figure 1 The crystal structure of RDX.

Crystal Structure of β -HMX

The crystal structure of β -HMX has been determined by X-ray and neutron diffraction^{3,4,5}. The compound crystallizes in the monoclinic space group $P2_1/c$. There are two molecules per unit cell and the molecules are centro-symmetric, Figure 2. Parameters of a unit cell are: $a = 6.54$, $b = 11.05$, $c = 8.70\text{\AA}$, $\beta = 124.3^\circ$.

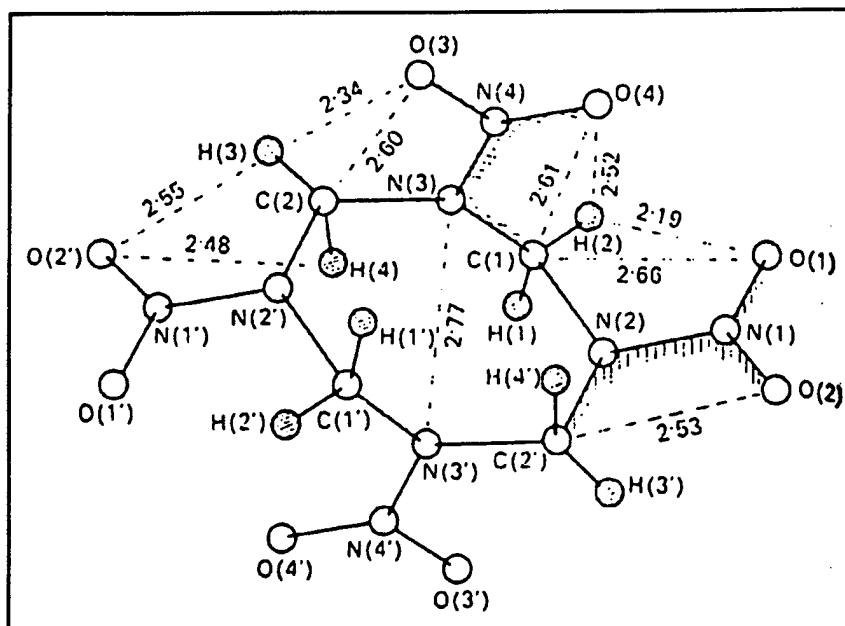


Figure 2 The crystal structure of β -HMX.

3. VECTOR AND TENSOR ANALYSIS IN THE NONORTHONORMAL SYSTEMS

The most important concept of tensor analysis is that the properties of any physical or geometrical quantity remain invariant under transformation of the coordinate system in which its properties have been originally described. In particular, considering crystal structures, the distance between atoms, angles between bonds, and the volume of a unit cell must be unchanged. When noncoplanar vectors a_i span a three-dimensional space ($i=1,2,3$), then a set of reciprocal vectors a_i^* exists, such that

$$a_i \cdot a_j^* = \delta_{ij} . \quad (1)$$

There are two different conventions for a definition of crystal parameters in the crystallographic literature⁶. In most textbooks, the direct unit cell parameters (axes and angles between them) are denoted $a, b, c, \alpha, \beta, \gamma$; the reciprocal unit cell parameters are denoted $a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*$. The basic relations between the basis vectors are:

$$\begin{aligned}
\mathbf{a}^* &= \frac{\mathbf{b} \times \mathbf{c}}{V}, \\
\mathbf{b}^* &= \frac{\mathbf{c} \times \mathbf{a}}{V}, \\
\mathbf{c}^* &= \frac{\mathbf{a} \times \mathbf{b}}{V},
\end{aligned} \tag{2}$$

$$V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}), \quad V^* = V^{-1},$$

where V is volume of a unit cell in the direct lattice, and V^* is volume of a unit cell in the reciprocal lattice. A metric tensor for the direct lattice is

$$\mathbf{g} = \begin{bmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{bmatrix}, \tag{3}$$

where each tensor element is a scalar product of the corresponding basis vectors. Similarly, the metric tensor for reciprocal lattice is

$$\mathbf{g}^* = \begin{bmatrix} \mathbf{a}^* \cdot \mathbf{a}^* & \mathbf{a}^* \cdot \mathbf{b}^* & \mathbf{a}^* \cdot \mathbf{c}^* \\ \mathbf{b}^* \cdot \mathbf{a}^* & \mathbf{b}^* \cdot \mathbf{b}^* & \mathbf{b}^* \cdot \mathbf{c}^* \\ \mathbf{c}^* \cdot \mathbf{a}^* & \mathbf{c}^* \cdot \mathbf{b}^* & \mathbf{c}^* \cdot \mathbf{c}^* \end{bmatrix}. \tag{4}$$

In our calculations we use another convention⁷. First we define a vector in the direct basis and in the reciprocal basis of the coordinate system:

$$\begin{aligned}
\mathbf{X} &= x^i \mathbf{a}_i, \\
\mathbf{X} &= x_i \mathbf{a}^i,
\end{aligned} \tag{5}$$

where \mathbf{a}_i are base vectors and \mathbf{a}^i are reciprocal base vectors, and $i=1,2,3$ for three-dimensional lattices. Subscripts denote covariant quantities, superscripts denote contravariant quantities, and, according to the Einstein notation, summation is implied over the repeated indices. The covariant

quantities transform as the base vectors, while contravariant quantities transform as the reciprocal base vectors. Transformation between base and reciprocal base vectors is given by

$$a^i = g^{ij} a_j, \quad a_i = g_{ij} a^j, \quad (6)$$

where $g_{..}$ and $g^{..}$ are two-covariant and two-contravariant metric tensors, respectively. Transformation of vector components is performed as follows

$$x^i = g^{ij} x_j, \quad x_i = g_{ij} x^j. \quad (7)$$

In the following formulae we list the most important relations between the metric tensors:

$$\begin{aligned} g_{ij} &= a_i \cdot a_j, & |g_{..}| &= |g^{..}|^{-1} = g, \\ g^{ij} &= a^i \cdot a^j, & g^i_j &= g_i^j = a^i \cdot a_j = \delta_j^i, \\ & & g_{ij} \cdot g^{jk} &= \delta_i^k. \end{aligned} \quad (8)$$

Volume of a unit cell in either basis can be expressed in terms of determinant of the appropriate metric tensor:

$$V = \sqrt{|g_{..}|}, \quad V^* = \sqrt{|g^{..}|}. \quad (9)$$

Scalar products include a metric tensor and can be calculated as follows:

$$(XY) = g_{mn} x^m y^n = g^{mn} x_m y_n = x^m y_m. \quad (10)$$

The following equations define vector products:

$$\begin{aligned} [XY]^r &= \epsilon^{mn} x_m y_n, \\ [XY]_r &= \epsilon_{mn} x^m y^n, \end{aligned} \quad (11)$$

where ϵ is Levi-Civita symbol, and

$$\varepsilon_{rmn} = g^{1/2} ; \quad \varepsilon^{rmn} = g^{-1/2} ; \quad (a)$$

$$\varepsilon_{rmn} = -g^{1/2} ; \quad \varepsilon^{rmn} = -g^{-1/2} ; \quad (b) \quad (12)$$

$$\varepsilon_{rmn} = 0 ; \quad \varepsilon^{rmn} = 0 ; \quad (c)$$

(a) *rmn* cyclic permutation of 1 2 3, (b) *rmn* cyclic permutation of 3 2 1, (c) for any two indices equal. Attention should be brought to the fact that when vectors *X* and *Y* are defined in the direct base, then the resultant of their vector product is in the reciprocal base, and *vice versa*. If needed, the indices may be raised or lowered by an appropriate metric tensor according to equations (7).

The next problem is the calculation of bond lengths. Let *X* be a vector connecting atoms A and B:

$$X = x^i a_i , \quad (13)$$

then the coordinates of the vector *X* are given as the difference between fractional coordinates of atoms A and B:

$$x^i = x_A^i - x_B^i . \quad (14)$$

The square of the length of the vector *X* is:

$$|X|^2 = g_{ij} x^i x^j , \quad (15)$$

which is equivalent to:

$$\begin{bmatrix} x^1 & x^2 & x^3 \end{bmatrix} \begin{bmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{bmatrix} \begin{bmatrix} x^1 \\ x^2 \\ x^3 \end{bmatrix} . \quad (16)$$

An angle between vectors *X* and *Y*, connecting atoms B and A and atoms B and C, is calculated according to the following formulae:

$$\begin{aligned} X &= x^i a_i, & x^i &= {}_A x^i - {}_B x^i, \\ Y &= y^i a_i, & y^i &= {}_C y^i - {}_B y^i, \end{aligned} \quad (17)$$

$$\cos \Theta = \frac{g_{ij} x^i y^j}{[g_{ij} x^i x^j]^{1/2} [g_{ij} y^i y^j]^{1/2}}.$$

Many physical properties are described by second order tensors, in particular by ellipsoids. Thus the last topic we address here is the computation of eigen-values and eigen-vectors of a quadratic form. Let us consider an eigen-problem for a two-covariant tensor β . In the oblique coordinate systems, the Lagrange multiplier λ is multiplied by the corresponding metric tensor, two-covariant in this case:

$$(\beta_{ij} - \lambda g_{ij}) x^i = 0, \quad (18)$$

where x^i are the coordinates of the eigen-vectors, which will be computed later. The above equation may be simplified by lowering indices of x :

$$x^i = g^{mi} x_m. \quad (19)$$

After substitution we obtain the following equation:

$$(\beta_{ij} g^{mi} - \lambda \delta_j^m) x_m = 0. \quad (20)$$

For a three-dimensional space the equation (20) represents a set of three linear homogenous equations for x_m . This set has nontrivial solutions only if the determinant of the coefficients vanishes:

$$|\beta_{ij} g^{mi} - \lambda \delta_j^m| = 0, \quad (21)$$

Further, this leads to a cubic equation in λ . In practice, we deal with physical quantities that are expressed by positive definite quadratic forms. Thus the solutions of equation (21) are real and positive. Substitution of $\lambda^{(r)}$ into equation (20) gives a set of x_m that determines an eigen-vector. For an ellipsoid, eigen-vectors point along principal axes, and eigen-values determine their lengths.

4. CALCULATIONS OF SECOND MOMENTS IN NQR SPECTRA

In this section we outline the procedure for calculating second moments of NQR lines for nuclei with spin $I = 1$, that was published by Shimon Vega⁸. The equations presented here can be found in that reference along with detailed derivations. Some equations are corrected for errors. We limit our discussion to a case where nuclei possess integer spins, asymmetric electric field gradient, and no external magnetic field is present. Thus, the energy of the system is given by a total Hamiltonian $\mathcal{H}_T = \mathcal{H}_Q + \mathcal{H}_D$ (*i.e.* sum of quadrupolar and dipolar Hamiltonians).

Several contributions to the second moment are expected. We consider interactions between completely equivalent nuclei, interactions between nuclei with the electric field gradient (EFG) tensors of the same magnitude but different orientation, and also we calculate second order contribution from nuclei with spin $I = 1/2$ (¹H).

NQR spectral lines may be either inhomogeneously or homogeneously broadened. The inhomogeneous broadening arises if there is a distribution of quadrupolar coupling constants. Such a distribution may occur when impurities are present in a crystal, and also when defects in the crystal lattice are abundant. Both factors will affect the EFG experienced by a nucleus contributing to the NQR signal; the effect will be most prominent in the ionic crystals where impurities and crystal imperfections alter significantly the electronic structure of the adjacent ions.

In the covalent crystals these effects are less significant, and the broadening origins mainly in dipolar interactions with neighboring nuclei in a molecule, which is homogeneous in nature. Thus it is convenient to characterize the line-shape by second moments.

The n^{th} central moment of a distribution $f(\omega)$ is

$$\langle \omega^n \rangle = \int_0^\infty \omega^n f(\omega) d(\omega) / \int_0^\infty f(\omega) d(\omega) , \quad (22)$$

and the n^{th} moment related to the center of a distribution is

$$\langle \Delta \omega^n \rangle = \int_0^\infty (\omega - \langle \omega \rangle)^n f(\omega) d(\omega) / \int_0^\infty f(\omega) d(\omega) . \quad (23)$$

In our case $f(\omega)$ is the line-shape function of a resonance signal:

$$f(\omega) = \gamma \hbar \sum_{a,b} |\langle I_r \rangle|^2 \delta(E_a - E_b - \hbar \omega) , \quad (24)$$

where ω is frequency in radians per seconds, γ is the gyromagnetic ratio, \hbar is Plank's constant, I_r is in the direction of r_f radiation, E_a and E_b represent energy of levels a and b , respectively. Summation is carried over all states present in the system. Thus, in general, several spectroscopic signals are included, while the shape function of one line at a time is desired. To make such a restriction, the Hamiltonian of the system is truncated, which means that the off-diagonal elements of \mathcal{H}_b except those connecting the degenerate states of \mathcal{H}_Q are excluded.

The quadrupolar Hamiltonian \mathcal{H}_Q is:

$$\begin{aligned} \mathcal{H}_Q &= \sum_i \mathcal{H}_{Qi} = \sum_i A_i [3I_{zi}^2 - I_i^2 + \eta(I_{xi}^2 - I_{yi}^2)] \\ A_i &= e^2 q_i Q_i / 4I_i(2I_i - 1) , \\ \eta &= (V_{xx} - V_{yy}) / V_{zz} , \quad V_{zz} = eq , \end{aligned} \quad (25)$$

where η is the asymmetry parameter, A is the quadrupole coupling constant, Q is the electric quadrupole moment, and $V_{..}$ are the principal values of the EFG tensor. The components of angular momentum are chosen along the eigen-vectors of the EFG tensor.

The dipolar Hamiltonian \mathcal{H}_D is

$$\mathcal{H}_D = \sum_i \mathcal{H}_{ij} = \hbar^2 \sum_{i>j} \left(\gamma_i \gamma_j / r_{ij}^3 \right) \left[\mathbf{I}_i \cdot \mathbf{I}_j - \left(3 / r_{ij}^2 \right) (\mathbf{I}_i \cdot \mathbf{r}_{ij}) (\mathbf{I}_j \cdot \mathbf{r}_{ij}) \right], \quad (26)$$

where \mathbf{r}_{ij} denotes vector connecting nuclei i and j . Further

$$\begin{aligned} \mathcal{H}_{ij} = & \left(\hbar^2 \gamma_i \gamma_j / r_{ij}^3 \right) [XOS_{ij} I_{xi} I_{xj} + YOS_{ij} I_{yi} I_{yj} \\ & + ZOS_{ij} I_{zi} I_{zj} - 3X_{ij} Y_{ij} (I_{xi} I_{yj} + I_{yi} I_{xj}) \\ & - 3X_{ij} Z_{ij} (I_{xi} I_{zj} + I_{zi} I_{xj}) - 3Y_{ij} Z_{ij} (I_{yi} I_{zj} + I_{zi} I_{yj})], \end{aligned} \quad (27)$$

$$\begin{aligned} X_{ij} &= \sin \theta_{ij} \cos \phi_{ij}, & XOS_{ij} &= 1 - 3X_{ij}^2, \\ Y_{ij} &= \sin \theta_{ij} \sin \phi_{ij}, & YOS_{ij} &= 1 - 3Y_{ij}^2, \\ Z_{ij} &= \cos \theta_{ij}, & ZOS_{ij} &= 1 - 3Z_{ij}^2, \end{aligned}$$

where θ denotes angle between vector \mathbf{r}_{ij} and z direction, and ϕ denotes angle between projection of \mathbf{r}_{ij} on the xy plane and x direction.

For completely equivalent nuclei the second moment is

$$\langle \Delta \omega^2 \rangle = - \frac{1}{2(2I+1) \hbar^2 \text{tr} [I_r]_{(2I+1)}^2} \sum_{j \neq i} \text{tr} [\mathcal{H}'_{ij} I_{ri} + I_{rj}]_{(2I+1)}^2, \quad (28)$$

where \mathcal{H}'_{ij} is a truncated Hamiltonian.

First the energies and eigen-functions of \mathcal{H}_Q for a single nucleus are calculated:

$$\begin{aligned} E_x &= A(1 - \eta) , & |x\rangle &= (1/\sqrt{2})(|+1\rangle - |-1\rangle) , \\ E_y &= A(1 + \eta) , & |y\rangle &= (1/\sqrt{2})(|+1\rangle + |-1\rangle) , \\ E_z &= -2A , & |z\rangle &= |0\rangle , \end{aligned} \quad (29)$$

Then this basis set is used for computation of energies and eigen-functions of \mathcal{H}_{Q_i} and \mathcal{H}_{Q_j} (for two nuclei i and j) :

$$\begin{aligned} E_{yy} &= 2A(1 + \eta) , & |yy\rangle &= |y\rangle_i |y\rangle_j , \\ E_{yx} &= E_{xy} = 2A , & |yx\rangle &= |y\rangle_i |x\rangle_j , & |xy\rangle &= |x\rangle_i |y\rangle_j , \\ E_{xx} &= 2A(1 - \eta) , & |xx\rangle &= |x\rangle_i |x\rangle_j , \\ E_{yz} &= E_{zy} = -A(1 - \eta) , & |yz\rangle &= |y\rangle_i |z\rangle_j , & |zy\rangle &= |z\rangle_i |y\rangle_j , \\ E_{zx} &= E_{xz} = -A(1 + \eta) , & |xz\rangle &= |x\rangle_i |z\rangle_j , & |zx\rangle &= |z\rangle_i |x\rangle_j , \\ E_{zz} &= -4A , & |zz\rangle &= |z\rangle_i |z\rangle_j , \end{aligned} \quad (30)$$

Elements of the truncated Hamiltonian \mathcal{H}_Q' are calculated in the new basis:

$$h_{23} = h_{32} = ZOS_{ij}, \quad h_{56} = h_{65} = XOS_{ij}, \quad h_{78} = h_{87} = YOS_{ij},$$

and for the transition $|y\rangle \leftrightarrow |z\rangle$ there are twelve elements of $(I_{xi} + I_{xj})$. All of them are equal to one.

Finally, after evaluation of the commutator and traces in Equation (28), the second moments for completely equivalent nuclei are:

$$\langle \Delta \omega^2 \rangle (|y\rangle \leftrightarrow |z\rangle) = \quad (32)$$

$$\frac{1}{12} \gamma^4 \hbar^2 \sum_{j \neq i} \left(1/r_{ij}^6 \right) \left(8 XOS_{ij}^2 + 4 YOS_{ij}^2 + 4 ZOS_{ij}^2 - 8 YOS_{ij} ZOS_{ij} \right),$$

where

$$\sum_{j \neq i} = \frac{2}{n} \left[\sum_{j > i}^n + \frac{1}{2} \sum_{j=n+1}^N \sum_{i=1}^n \right]. \quad (33)$$

Here, the summation is carried over all equivalent nuclei in a unit cell (n), and a total of N nuclei are included in the calculations. The meaning of this sum is that there is $N-1$ interactions between one nucleus and all others.

Next we include equivalent nuclei with different directions of the EFG tensors residing in two sites I and II. The sum in Equation (28) must be replaced by $\sum_{j>i} + \sum_{i>k} + \sum_{k>l}$, where

i and j represent nuclei in site I, while k and l represent those in site II. Now there are following contributions to the second moment: $\langle \Delta \omega^2 \rangle (I, I)$, $\langle \Delta \omega^2 \rangle (II, II)$, $\langle \Delta \omega^2 \rangle (I, II)$, where

$$\langle \Delta \omega^2 \rangle (I, I) = \langle \Delta \omega^2 \rangle \cos^2 \alpha^I / (\cos^2 \alpha^I + \cos^2 \alpha^{II}), \quad (36)$$

and α^I and α^{II} are the angles between direction of γ radiation and direction of I_z for nuclei in sites I and II.

The calculation of the second moments for nuclei in two different sites (I, II) requires a revision of the coordinate systems. So far all the angular momentum operators have been written in the coordinate system of one site, which was common for all nuclei under consideration and was determined by a set of eigen-vectors of the EFG tensor. In order to apply

the above formulae, the vector quantities for the nuclei in both sites must be referred to the same coordinate system. Thus the angular momentum operators in the coordinate system of site I are transformed to the coordinate system of site II:

$$I_{rk}^I = \sum_{r'} R_{rr'} I_{r'k}^II, \quad (37)$$

where $R_{rr'}$ is the transformation matrix between the coordinate systems defined by the principal axes of EFG tensors of the nuclei in site I and site II. To further facilitate calculations, we transform coordinates from the crystallographic axes system to the orthonormal system of the same system as defined for the angular momentum operators. The derivation of both transformation matrices are given in Appendices A and B.

The nonvanishing elements of the truncated Hamiltonian \mathcal{H}_q' and $(I_{ri} + I_{rk})'$ are

$$\begin{aligned} h_{23} = h_{32} &= R_{zz} Z O S_{ik} - 3 R_{yz} Y_{ik} Z_{ik} - 3 R_{xz} X_{ik} Z_{ik}, \\ h_{56} = h_{65} &= R_{xx} X O S_{ik} - 3 R_{yx} X_{ik} Y_{ik} - 3 R_{zx} X_{ik} Z_{ik}, \\ h_{78} = h_{87} &= R_{yy} Y O S_{ik} - 3 R_{xy} X_{ik} Y_{ik} - 3 R_{zy} Y_{ik} Z_{ik}, \end{aligned} \quad (38)$$

$$\begin{aligned} i_{15} = i_{51} = i_{37} = i_{73} = i_{69} = i_{96} &= \cos \alpha^I, \\ i_{16} = i_{61} = i_{28} = i_{82} = i_{59} = i_{95} &= \cos \alpha^{II}. \end{aligned}$$

The contribution to the second moment from nuclei in sites I and II is

$$\langle \Delta \omega^2 \rangle (I, II) (|y\rangle \leftrightarrow |z\rangle) = \quad (39)$$

$$\begin{aligned} &\frac{1}{6} \gamma^4 \hbar^2 \sum_k \left(1/r_{ik}^6 \right) [2h_{23}^2 + 2h_{78}^2 + 4h_{56}^2 \\ &- 8 \cos \alpha^I \cos \alpha^{II} (\cos^2 \alpha^I + \cos^2 \alpha^{II})^{-1} h_{23} h_{78}], \end{aligned}$$

Dipole-dipole interactions between nitrogen nuclei and protons quite often contribute to the second moment of an NQR signal. However, in the absence of external magnetic field and for nonzero asymmetry parameter, this contribution vanishes in the first order. Thus, only the second order contribution is considered:

$$\begin{aligned} \langle \Delta \omega^2 \rangle^{NH} (|y\rangle \leftrightarrow |z\rangle) = & \\ \frac{\gamma_N^4 \gamma_H^4 \hbar^6}{4(E_x - E_y)^2} \sum_{s>t} \left(\frac{1}{r_{is}^6 r_{it}^6} \right) \{ & 2ZOS_{is}^2 ZOS_{it}^2 \\ + 9[ZOS_{is}^2 (X_{it}^2 + Y_{it}^2) + ZOS_{it}^2 (X_{is}^2 + Y_{is}^2)] & \\ + 81(X_{is}^2 X_{it}^2 + Y_{is}^2 Y_{it}^2 + X_{is}^2 Y_{it}^2 + Y_{is}^2 X_{it}^2) \}. & \end{aligned} \quad (40)$$

The above equation ends the list of the contributions that may be important for the case of nuclei with spin $I = 1/2$, nonzero asymmetry parameter, and when NQR signals are measured in the absence of external magnetic field.

5. NUMERICAL CALCULATIONS

Programs for the calculations of second moments of NQR signals are written in MATLAB, Version 4.0, released by The Math Work, Inc. in 1993. The most important programs are listed in the Appendix C. The computations have been performed on a personal computer, Gateway 2000.

Two files, rdx.m and hmx_b.m, include crystallographic data from literature and provide input to all other programs. The calculation of second moments of NQR signals also requires knowledge of the directions of the principal axes of electric field gradient tensors. For RDX and β -HMX the EFG tensors have not been measured. However, the orientation of the tensors can be determined from the electronic structure of the molecules of RDX and β -HMX⁹. Thus, Y axis coincides with N-N bond in N-NO₂ group, X axis is perpendicular to Y, and it is in the plane of N-NO₂ group. Axis Z is perpendicular to XY plane.

6. RESULTS AND DISCUSSION

This section presents numerical results of the second moment calculations for β -HMX and RDX. In most computations the nuclei in the translation limits $t=3$ were included. Translation limits refer to the number of unit cells in each crystallographic direction (positive and negative) taken from an arbitrary unit cell chosen as an origin. Thus $(2t + 1)^3$ unit cells were considered. Table 1 shows an example of how fast convergence is achieved. The direction of rf radiation is fixed. The value of $\langle \omega^2 \rangle^{1/2}$ stops changing for $t > 3$. Thus, for calculations of second moments in the first order this limit was used.

Table 1. Data for β -HMX. The convergence of the second moments calculations versus the translation limits, t . The angles between the direction of rf radiation and the X axis of the EFG tensors for sites I and II are given by cosines $\cos I$ and $\cos II$, respectively

t	$\cos I$	$\cos II$	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{II,II}$	$\langle \omega^2 \rangle^{1/2}$
0	0.800	-0.875	630	9934	3606	119
1	0.800	-0.875	3613	10191	3858	133
2	0.800	-0.875	3708	10219	3886	133
3	0.800	-0.875	3729	10224	3891	134
4	0.800	-0.875	3736	10226	3893	134
5	0.800	-0.875	3738	10226	3894	134

Data in the two following tables are sorted according to the largest contributions to the second moment (SM) from the dipolar interactions between nuclei i and j . Only the largest contributions are listed. Note the difference between SM and $\langle \omega^2 \rangle$. SM is the contribution to the second moment from one pair of nuclei only, while $\langle \omega^2 \rangle$ is obtained by averaging over all atoms. The nuclei i are in an arbitrarily chosen unit cell taken as the origin. The nuclei j are either in the original unit cell or in the neighboring unit cell with the translation parameters m , n , and p . The distance between nuclei i and j is r_{ij} . The direction of rf radiation in the orthonormal system is $[1 -2 6]$.

Table 2. Data for β -HMX. Contributions to the second moments from completely equivalent nuclei N(2).

i - j	m n p	r_{ij} [Å]	SM [rad ² /sec ²]
2 - 4	0 0 0	3.935	4868.26
1 - 3	0 0 0	3.935	3242.58
2 - 4	1 0 1	4.358	1025.50
1 - 3	-1 0 -1	4.358	604.78
2 - 4	1 0 0	5.008	235.80
1 - 3	-2 0 -1	7.071	202.15
2 - 4	2 0 1	7.071	165.75
2 - 2	1 0 0	6.540	163.05
2 - 2	-1 0 0	6.540	163.05
1 - 1	1 0 0	6.540	163.05
1 - 1	-1 0 0	6.540	163.05
1 - 3	-1 0 0	5.008	73.79
2 - 4	-1 0 0	9.562	32.96
1 - 3	1 0 0	9.562	29.16
2 - 2	0 0 1	8.700	14.77
2 - 2	0 0 -1	8.700	14.77
1 - 1	0 0 1	8.700	14.77
1 - 1	0 0 -1	8.700	14.77
2 - 2	-2 0 -1	10.887	12.65
1 - 1	2 0 1	10.887	12.65
2 - 2	2 0 1	10.887	12.65
1 - 1	-2 0 -1	10.887	12.65
1 - 3	-1 -1 -1	11.355	8.85
1 - 3	-3 0 -1	12.906	5.48
2 - 4	1 -1 0	11.620	5.28
2 - 4	3 0 1	12.906	5.00
1 - 3	-1 -1 0	11.620	4.97
2 - 4	1 1 1	12.380	4.88
2 - 4	0 -1 0	11.199	4.65

Table 3. Data for β -HMX. Contributions to the second moments from equivalent nuclei N(2) with the different directions of the EFG tensors.

i - j	m n p	r_{ij} [Å]	SM [rad ² /sec ²]
3 - 4	1 -1 0	5.774	238.78
1 - 2	-1 -1 -1	5.774	238.78
3 - 4	1 0 0	5.774	238.78
1 - 2	-1 0 -1	5.774	238.78
4 - 1	0 1 0	6.608	137.91
2 - 3	0 0 1	6.608	137.91
4 - 1	0 1 1	6.608	114.58
2 - 3	0 0 0	6.608	114.58
2 - 3	0 1 0	7.472	59.85
4 - 1	0 0 1	7.472	59.85
2 - 3	0 1 1	7.472	52.29
4 - 1	0 0 0	7.472	52.29
2 - 1	1 1 1	5.774	44.44
4 - 3	-1 0 0	5.774	44.44
4 - 3	0 1 0	7.470	26.89
2 - 1	0 0 1	7.470	26.89
4 - 1	-1 1 0	7.374	20.35
2 - 3	1 0 1	7.374	20.35
2 - 1	0 1 1	7.470	17.65
4 - 3	0 0 0	7.470	17.65
2 - 1	0 0 0	8.571	16.16
4 - 3	0 1 1	8.571	16.16
4 - 3	0 0 1	8.571	15.46
2 - 1	0 1 0	8.571	15.46
3 - 2	-1 0 -1	7.374	14.15
1 - 4	1 -1 0	7.374	14.15
3 - 2	1 0 0	7.374	14.15
1 - 4	-1 -1 -1	7.374	14.15
1 - 4	0 -1 0	6.608	13.65
3 - 2	0 0 -1	6.608	13.65

Table 4. Data for β -HMX. Contribution to the second moment in the first order for N(2) for different directions of rf radiation; translation limits $t = 3$; angles between direction of rf radiation and X axis of the EFG tensors of nuclei in sites I and II are given by cosines cosI and cosII, respectively; $\langle \omega^2 \rangle$ is in units of $[\text{rad}^2/\text{sec}^2]$.

cosI	cosII	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{II,II}$	$\langle \omega^2 \rangle^{1/2}$
-0.910	0.413	2583	3874	5675	110
-0.940	0.179	2482	4507	6602	117
-0.864	-0.213	2264	4402	6449	115
-0.961	0.370	2562	4067	5958	112
-0.996	0.122	2449	4602	6741	117
-0.907	-0.286	2236	4249	6225	113
-0.933	0.275	2528	4298	6296	115
-0.965	0.031	2403	4666	6836	118
-0.884	-0.359	2203	4010	5875	110
-0.371	0.759	2593	902	1321	69
-0.447	0.268	2617	3436	5034	105
-0.298	-0.539	2164	1094	1602	70
-0.535	0.892	2617	1233	1807	75
-0.894	0.201	2498	4446	6513	116
-0.365	-0.797	2188	810	1187	65
-0.426	0.499	2645	1971	2888	87
-0.555	-0.152	2252	4344	6363	114
-0.324	-0.870	2215	570	835	60
0.625	0.545	2127	2653	3887	93
0.707	0.106	2309	4569	6693	116
0.530	-0.559	2647	2212	3241	90
0.784	0.537	2142	3180	4658	100
0.970	-0.036	2406	4664	6833	118
0.617	-0.766	2642	1838	2692	85
0.686	0.298	2194	3927	5753	109
0.800	-0.230	2525	4315	6321	115
0.566	-0.844	2628	1449	2123	79

Table 5. Data for β -HMX. Contribution to the second moment in the first order for N(3) for different directions of γ radiation; translation limits $t = 3$; angle between direction of γ radiation and X axis of the EFG tensors of nuclei in sites I and II are given by cosines cosI and cosII, respectively; $\langle \omega^2 \rangle$ is in units of $[\text{rad}^2/\text{sec}^2]$.

cosI	cosII	$\langle \omega^2 \rangle^{\text{I,II}}$	$\langle \omega^2 \rangle^{\text{I,I}}$	$\langle \omega^2 \rangle^{\text{II,II}}$	$\langle \omega^2 \rangle^{1/2}$
-0.910	0.882	3731	11586	4410	140
-0.940	0.964	3731	10945	4166	137
-0.864	0.969	3728	9956	3789	132
-0.961	0.885	3730	12157	4627	143
-0.996	0.974	3731	11485	4371	140
-0.907	0.973	3730	10445	3976	135
-0.933	0.799	3727	12958	4932	147
-0.965	0.881	3729	12246	4661	144
-0.884	0.891	3731	11138	4239	138
-0.371	0.372	3731	11213	4268	139
-0.447	0.588	3718	8231	3133	123
-0.298	0.548	3673	5135	1954	104
-0.535	0.394	3715	14562	5542	154
-0.894	0.939	3730	10684	4067	136
-0.365	0.574	3697	6471	2463	112
-0.426	0.164	3612	19587	7455	175
-0.555	0.387	3709	15124	5756	157
-0.324	0.396	3724	9038	3440	127
0.625	-0.588	3730	11906	4532	142
0.707	-0.555	3721	13899	5290	151
0.530	-0.278	3667	17627	6709	167
0.784	-0.843	3730	10430	3970	135
0.970	-0.890	3729	12197	4642	143
0.617	-0.405	3701	15700	5975	159
0.686	-0.858	3722	8759	3334	126
0.800	-0.875	3729	10224	3891	134
0.566	-0.471	3725	13261	5047	148

Table 6. Data for RDX. Contribution to the N(1) second moment, to first order, for two directions of rf radiation; translation limits $t = 3$; angle between the direction of rf radiation and X axis of the EFG tensors of nuclei in two different sites I and II are given by cosines $\cos I$ and $\cos II$, respectively; $\langle \omega^2 \rangle$ is in units of $[\text{rad}^2/\text{sec}^2]$.

$\cos I$	$\cos II$	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{1/2}$
0.732	0.885	2856	210	55
0.704	0.838	2849	232	56
0.625	0.728	2846	257	56
0.501	0.565	2849	287	56
0.362	0.389	2862	320	56
0.865	0.969	2858	212	55
0.861	0.939	2854	234	56
0.783	0.823	2853	260	56
0.631	0.630	2860	291	56
0.458	0.422	2878	326	57
0.959	0.998	2858	213	55
0.972	0.977	2855	235	56
0.898	0.859	2857	262	56
0.732	0.653	2868	294	56
0.536	0.431	2891	330	57
0.982	0.956	2854	214	55
0.993	0.924	2853	237	56
0.922	0.807	2857	264	56
0.764	0.615	2870	297	56
0.575	0.409	2899	333	57
0.945	0.861	2848	214	55
0.939	0.812	2847	237	56
0.869	0.701	2852	265	56
0.736	0.539	2868	298	56
0.575	0.365	2900	335	57
-0.271	-0.347	2845	314	56
-0.091	-0.186	2843	330	56
0.140	0.024	2927	420	58

Table 7. Data for RDX. Contribution to the N(2) second moment, to first order, for different directions of rf radiation; translation limits $t = 3$; angle between direction of rf radiation and X axis of the EFG tensors of nuclei in sites two different sites I and II are given by cosines $\cos I$ and $\cos II$, respectively; $\langle \omega^2 \rangle$ is in units of $[\text{rad}^2/\text{sec}^2]$.

$\cos I$	$\cos II$	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{1/2}$
-0.592	-0.483	1808	554	49
-0.579	-0.674	1810	437	47
-0.524	-0.846	1856	325	47
-0.432	-0.957	1932	241	47
-0.326	-0.997	2037	192	47
-0.395	-0.419	1806	535	48
-0.363	-0.632	1882	393	48
-0.294	-0.831	1998	273	48
-0.198	-0.952	2117	201	48
-0.102	-0.985	2273	175	49
-0.143	-0.317	1940	463	49
-0.076	-0.529	2180	331	50
0.011	-0.734	2348	236	51
0.097	-0.864	2446	200	51
0.161	-0.905	2511	202	52
0.119	-0.192	2716	521	57
0.217	-0.376	2756	407	56
0.314	-0.562	2753	309	55
0.382	-0.695	2740	295	55
0.412	-0.758	2753	301	55
0.341	-0.071	2521	758	57
0.449	-0.220	2743	569	58
0.542	-0.375	2783	468	57
0.596	-0.503	2815	459	57
0.607	-0.585	2834	444	57
0.491	0.967	1909	223	46
0.561	0.922	1872	226	46
0.622	0.820	1845	232	46
0.648	0.648	1879	256	46
0.627	0.428	1879	368	47

Table 8. Data for RDX. Contribution to the N(3) second moment, to first order, for different directions of rf radiation; translation limits $t = 3$; angle between direction of rf radiation and X axis of the EFG tensors of nuclei in two different sites sites I and II are given by cosines cosI and cosII, respectively; $\langle \omega^2 \rangle$ is in units of $[\text{rad}^2/\text{sec}^2]$.

cosI	cosII	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{1/2}$
0.633	-0.608	2745	366	56
0.751	-0.429	2783	446	57
0.834	-0.195	2807	526	58
0.856	0.053	2828	420	57
0.825	0.266	2897	456	58
0.460	-0.727	2776	262	55
0.578	-0.549	2950	318	57
0.669	-0.290	3083	376	59
0.697	-0.005	3083	664	61
0.670	0.236	3047	559	60
0.230	-0.814	2773	174	54
0.324	-0.643	3094	209	57
0.408	-0.378	3388	365	61
0.449	-0.073	3331	651	63
0.448	0.185	3100	604	61
-0.017	-0.842	2919	138	55
0.040	-0.678	3093	177	57
0.105	-0.426	3324	316	60
0.159	-0.135	3548	561	64
0.194	0.121	3023	594	60
-0.232	-0.816	2783	157	54
-0.203	-0.658	2907	225	56
-0.156	-0.433	2987	354	58
-0.097	-0.177	2973	480	59
-0.040	0.058	3497	518	63
-0.915	-0.280	2694	382	55
-0.942	-0.410	2543	336	54
-0.929	-0.552	2289	268	51
-0.851	-0.678	2531	222	52
-0.711	-0.754	2896	211	56

In Table 9 we list the powder average of second moments calculated for β -HMX and RDX. The directions of rf radiation were represented by vectors from the center of a cube to the nodes on its grid. The grid on each wall was 6×6 .

Table 9. Data for β -HMX and RDX. Powder average of second moments.

β -HMX				
	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{II,II}$	$\langle \omega^2 \rangle^{1/2}$
N(2)	2418	3910	5727	110
N(3)	3660	10843	4127	133

RDX			
	$\langle \omega^2 \rangle^{I,II}$	$\langle \omega^2 \rangle^{I,I}$	$\langle \omega^2 \rangle^{1/2}$
N(1)	2906	244	56
N(2)	2243	454	52
N(3)	2857	367	57

The contributions SM to the second moment from completely equivalent nuclei and from equivalent nuclei with the different directions of the EFG tensors decrease rapidly with increasing distance (Tables 2 and 3). The angular factor influences the value of SM by approximately one order of magnitude for atoms separated by the same distance (Table 3). For β -HMX the contributions from completely equivalent nuclei are larger than those with the different directions of the EFG tensors. The values of $\langle \omega^2 \rangle^{I,I}$ and $\langle \omega^2 \rangle^{II,II}$ are larger than the value of $\langle \omega^2 \rangle^{I,II}$, which also is related to the distance, since intramolecular distances are shorter than intermolecular ones, and only completely equivalent nuclei are in the same molecule. Thus these atoms contribute the most to the second moment.

For β -HMX the value of $\langle \omega^2 \rangle^{1/2}$ is larger for N(3) than for N(2), which is explained by the difference in the intramolecular distances between atoms related by center of inversion. They are 2.77 and 3.94 Å for N(2) and N(3), respectively.

The dependence between values of $\langle \omega^2 \rangle^{I,II}$, $\langle \omega^2 \rangle^{I,I}$, and $\langle \omega^2 \rangle^{II,II}$, $\langle \omega^2 \rangle^{1/2}$ on direction of rf radiation is given in Tables 4 and 5 for β -HMX, and in Tables 6, 7, and 8 for RDX. The angular factor changes the value of $\langle \omega^2 \rangle^{1/2}$ by less than two.

In comparison to β -HMX the second moments $\langle \omega^2 \rangle^{1/2}$ for RDX are significantly smaller. Especially, the contribution from the completely equivalent nuclei are almost irrelevant. Again, this is due to the large distances, since there is no equivalent nuclei in the same molecule.

The linewidths of ^{14}N NQR signals for nitrogen nuclei in β -HMX are 1.4 kHz and 2.3 kHz. For RDX the observed linewidths range from 180 Hz to 490 Hz. The room temperature data are given in Table 10.

Table 10. ^{14}N NQR data for nitrogen atoms of β -HMX and RDX.

β -HMX	
$\nu_- = 3.737 \text{ MHz}$	$\Delta\nu = 1.4 \text{ kHz}$
$\nu_- = 3.623 \text{ MHz}$	$\Delta\nu = 2.3 \text{ kHz}$
RDX	
$\nu_- = 3.458 \text{ MHz}$	$\Delta\nu = 0.49 \text{ kHz}$
$\nu_- = 3.410 \text{ MHz}$	$\Delta\nu = 0.35 \text{ kHz}$
$\nu_- = 3.359 \text{ MHz}$	$\Delta\nu = 0.43 \text{ kHz}$
$\nu_+ = 5.24 \text{ MHz}$	$\Delta\nu = 0.43 \text{ Hz}$
$\nu_+ = 5.19 \text{ MHz}$	$\Delta\nu = 0.18 \text{ Hz}$
$\nu_+ = 5.04 \text{ MHz}$	$\Delta\nu = 0.38 \text{ Hz}$

The contributions to the second moment discussed above do not explain the experimentally observed linewidths. Thus the interactions between nitrogens and hydrogens are considered. In the absence of the external magnetic field there is no contribution to the second moment from the N-H dipolar interaction to the first order. However, the second order contribution may be significant because of the close distances between nitrogen and hydrogen atoms (Table 11 and 12).

Table 11. Data for β -HMX. The distance between ring nitrogen atoms and the closest hydrogen atoms, in Angstroms.

N(2) - H(1)	2.0854
N(2) - H(2)	2.0870
N(2) - H(3')	2.1083
N(2) - H(4')	2.1145
N(3) - H(1)	2.0671
N(3) - H(2)	2.1181
N(3) - H(3)	2.0937
N(3) - H(4)	2.0479

Table 12. Data for RDX. The distance between ring nitrogen atoms and the closest hydrogen atoms, in Angstroms.

N(1) - H(1)	2.0781
N(1) - H(2)	2.1038
N(1) - H(5)	2.0849
N(1) - H(6)	2.0977
N(2) - H(1)	2.0372
N(2) - H(2)	2.0869
N(2) - H(3)	2.1036
N(2) - H(4)	2.0643
N(3) - H(3)	2.1027
N(3) - H(4)	2.0598
N(3) - H(5)	2.0475
N(3) - H(6)	2.0841

The second order contributions $\langle \omega^2 \rangle^{1/2}(\text{NH})$ for β -HMX are presented in Table 13.

Table 13. Second order contributions to $\langle \omega^2 \rangle^{1/2}(\text{NH})$ for β -HMX.

t	N(2)	N(3)
	rad/s	rad/s
0	34	35
1	175	183
2	376	392
3	624	649

However, convergence is still not reached for $t = 3$. The computations were not continued because of the very long program run time. The values of $\langle \omega^2 \rangle^{1/2}(\text{NH})$ are much larger then $\langle \omega^2 \rangle^{1/2}$ calculated in the first order.

7. SUMMARY

This work focused on the calculations of second moments of ^{14}N NQR signals for two explosive materials, β -HMX and RDX. Several contributions were considered. Computations included interactions between completely equivalent nuclei, interactions between nuclei with the EFG tensors of the same magnitude but different orientation, and the second order contribution from heteronuclear dipolar interactions.

The calculations of second moments to the first order show that $\langle \omega^2 \rangle^{1/2}$ for β -HMX is larger than $\langle \omega^2 \rangle^{1/2}$ for RDX by a factor of two. The most significant difference is in the contributions from the completely equivalent nuclei, which are almost negligible for RDX.

In all the calculations of $\langle \omega^2 \rangle^{1/2}$ it was evident that the distance between interacting nuclei is the most significant factor. The angular factor influenced the value of SM by less than one order of magnitude for nuclei separated by the same distance.

The numerical results of the calculations of second moments presented in this work do not account for the experimentally observed linewidths of ^{14}N NQR signals. However, the second order contribution from heteronuclear dipolar interactions for β -HMX is significant, even though the convergence was not reached. Thus, the heteronuclear dipolar interactions between nitrogens and hydrogens may be important factors contributing to the second moments. It might be confirmed by the ^{14}N NQR study of deuterated samples of the explosive materials.

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ABBREVIATIONS

a, b, c	unit cell parameters
A	quadrupole coupling constant
E	energy
EFG	Electric Field Gradient
g	metric tensor
HMX	cyclotetramethylene tetranitramine
I	angular momentum
NQR	Nuclear Quadrupole Resonance
R	transformation matrix
RDX	cyclotrimethylene-trinitramine
rf	radio frequency
Q	electric quadrupole moment
$V_{..}$	principal values of an electronic field gradient tensor
α, β, γ	unit cell parameters (angles)
δ_{ij}	Kronecker delta
ϵ	Levi-Civita symbol
η	asymmetry parameter
γ	magnetogyric ratio
\hbar	Planck's constant
\mathcal{H}	Hamiltonian
λ	Lagrange multiplier
$\langle \Delta\omega^2 \rangle$	second moment

APPENDIX A

The transformation matrix between the coordinate systems defined by the principal axes of EFG tensors.

In this appendix we derive the transformation matrix between the coordinate systems defined by the principal axes of EFG tensors of the nuclei in the magnetically non-equivalent sites. Let vectors

$$(\vec{e}_i)_{i=1}^3, \quad (\vec{f}_i)_{i=1}^3, \quad (41)$$

denote eigen-vectors of EFG tensors in site I and site II. Next we write a tensor

$$E = \begin{bmatrix} e_1^1 & e_1^2 & e_1^3 \\ e_2^1 & e_2^2 & e_2^3 \\ e_3^1 & e_3^2 & e_3^3 \end{bmatrix}, \quad (42)$$

where the elements of each row are the components of an eigen-vector of the EFG tensor in crystallographic axes system. Similarly, the one-covariant one-contravariant tensor F for site II is constructed, and the eigen-vectors can be written as

$$\begin{aligned} \vec{e}_i &= \sum_{k=1}^3 E_i^k \vec{a}_k, \\ \vec{f}_i &= \sum_{k=1}^3 F_i^k \vec{a}_k. \end{aligned} \quad (43)$$

Further

$$\begin{aligned}
e_i &= E_i^k a_k, \\
(E_j^i)^{-1} e_i &= (E_j^i)^{-1} E_i^k a_k, \\
(E_j^i)^{-1} e_i &= \delta_j^k a_k, \\
a_j &= (E_j^i)^{-1} e_i, \\
f_i &= F_i^j a_j, \\
f_i &= F_i^j (E_j^k)^{-1} e_k, \\
f_i &= (F \cdot E^{-1})_i^k e_k, \\
e_m &= (E \cdot F^{-1})_m^i f_i, \\
R &= E \cdot F^{-1}.
\end{aligned} \tag{44}$$

Thus the matrix R transforms the base vectors e into f .

APPENDIX B

The transformation of x, y, z coordinates in direct lattice to the orthonormal system defined by the principal directions of an EFG tensor.

First we define a vector X in the crystallographic axes system a_i

$$X = x^i a_i.$$

Let vector Y be the same vector but defined in the orthonormal system e_i determined by the principal directions of an EFG tensor.

$$Y = y^i e_i.$$

The relation between two sets of the base vectors is

$$e_i = E_i^k a_k,$$

(see Appendix A for the definition of tensor E). If vectors X and Y are equal then

$$x^i a_i = y^i e_i,$$

$$x^i a_i = y^i E_i^k a_k,$$

$$x^i a_i \cdot a^j = y^i E_i^k a_k \cdot a^j,$$

$$x^i \delta_i^j = y^i E_i^k \delta_k^j,$$

$$x^j = y^i E_i^j,$$

$$(E_j^k)^{-1} = y^i \delta_i^k,$$

$$y^k = (E_j^k)^{-1} x^j.$$

Thus the tensor E^{-1} transforms coordinates from the crystallographic system a_i to the orthonormal system e_i .

APPENDIX C

Listing of programs

```
% *** hmx_b.m ***      Jolanta M. Snowel      January 26, 1995
%
% This program contains the direct unit cell axes, fractional atom coordinates
% in direct lattice, anisotropic temperature factors.
% It calculates the reciprocal metric tensor and reciprocal unit cell parameters.
% In general calculations are performed in a non-orthogonal basis.
%
% g - direct metric tensor
% G - reciprocal metric tensor
% a, b, c, alpha, beta, gamma - direct unit cell parameters
% ar, br, cr, Alpha, Beta, Gamma - reciprocal unit cell parameters
%
%   crystal: HMX_B
%
%   Chang S. Choi, Henry P. Boutin
%   Acta Cryst. 1970, B26, 1235-1240.

a=6.54; b=11.05; c=8.7; alpha=pi/2; beta=(124.3/360)*(2*pi); gamma=pi/2;
%beta=(124.3/360)*(2*pi);
g=[ a*a a*b*cos(gamma) a*c*cos(beta)
    b*a*cos(gamma) b*b b*c*cos(alpha)
    c*a*cos(beta) c*b*cos(alpha) c*c ];

G=inv(g);

ar=sqrt(G(1,1)); br=sqrt(G(2,2)); cr=sqrt(G(3,3));

Alpha=acos(G(2,3)/(sqrt(G(2,2))*sqrt(G(3,3))));
Beta=acos(G(1,3)/(sqrt(G(1,1))*sqrt(G(3,3))));
Gamma=acos(G(1,2)/(sqrt(G(1,1))*sqrt(G(2,2))));

data = [
-5928   -21   -2920   1092 504 651 61 148 242
-3482  -249  -2058   1199 363 617 -62 281 7
-188   1228  -377   1366 277 566 -26 482 -75
-1092  2023   316   1717 279 834 52 815 -39
-6885   735  -4182   1602 600 1049 190 73 2
-6991  -598  -2372   1708 823 1282 -237 1121 -104
422    2460  1818   3062 585 1361 -53 1155 -456
-3290  2206  -609   1883 603 1200 398 914 28
```

```

-1967    660    -2158    1103 357 467 -27 456 -57
2448 1    147     547    1865 247 755 -102 840 -31
-879     218    -2623    3247 585 1081 27 1623 -183
-3146    1326    -3223    2320 818 906 -231 383 207
3322     2031    1130     1478 636 1961 80 310 -111
2793     867     -494     3518 1199 1008 212 1520 -1

```

```
];
```

```
xyz=data(:,1:3); xyz=0.0001*xyz;
```

```
% B - thermal parameter tensor. It must be transformed to beta form:
```

```
%
```

```
% exp(-(B11*h^2 + B22*k^2 + B33*l^2 + 2*B12*h*k + 2*B13*h*l + 2*B23*k*l))
```

```
Bm =0.00001*data(:, 4:9); clear data;
```

```
Bm(:,4:6) = Bm(:,4:6)/2;
```

```
*****
*****
```

```
% *** rdx.m *** Jolanta M. Snowel May 15, 1995
```

```
%
```

```
% This program contains the direct unit cell axes, fractional atom coordinates
```

```
% in direct lattice, anisotropical temperature factors.
```

```
% It calculates the reciprocal metric tensor and reciprocal unit cell parameters.
```

```
% In general calculations are performed in a non-orthogonal basis.
```

```
%
```

```
% g - direct metric tensor
```

```
% G - reciprocal metric tensor
```

```
% a, b, c, alpha, beta, gamma - direct unit cell parameters
```

```
% ar, br, cr, Alpha, Beta, Gamma - reciprocal unit cell parameters
```

```
%
```

```
% crystal: RDX
```

```
%
```

```
% Chang S. Choi, E. Prince
```

```
% Acta Cryst. 1972, B28, 2857-2862.
```

```
a=13.182; b=11.574; c=10.709; alpha=pi/2; beta=pi/2; gamma=pi/2;
```

```
Z_au = 8; % number of asymmetric units
```

```
g=[ a*a a*b*cos(gamma) a*c*cos(beta)
    b*a*cos(gamma) b*b b*c*cos(alpha)
```

```

c*a*cos(beta) c*b*cos(alpha) c*c ];

G=inv(g);

ar=sqrt(G(1,1)); br=sqrt(G(2,2)); cr=sqrt(G(3,3));

Alpha=acos(G(2,3)/(sqrt(G(2,2))*sqrt(G(3,3))));
Beta=acos(G(1,3)/(sqrt(G(1,1))*sqrt(G(3,3))));
Gamma=acos(G(1,2)/(sqrt(G(1,1))*sqrt(G(2,2))));

data = [
1839 3578 4400 322 297 206 -70 -69 7
503 2440 3395 233 145 344 8 -1 -17
1487 3813 2159 252 332 175 -34 34 -31
1761 4360 3330 267 266 251 -109 1 0
877 2996 4537 295 210 250 14 33 9
536 3222 2329 211 228 274 15 -35 -37
2260 5379 3346 217 241 348 -55 79 -26
155 3525 5294 455 322 256 157 104 77
-333 3875 2078 284 306 316 72 -72 -53
2270 5932 2388 566 330 407 -122 82 68
2649 5687 4338 342 330 417 -86 -13 -131
-693 3142 5262 333 718 426 138 153 156
454 4271 5990 894 381 258 251 57 -53
-1121 3534 2504 246 572 584 44 -62 22
-236 4691 1390 644 441 415 185 -91 62
2401 2944 4226 372 532 564 -14 -128 141
2013 4068 5244 762 560 270 -201 -127 -59
-261 2117 3540 371 433 597 -146 -18 16
1015 1728 3192 464 263 594 89 -16 -114
2052 3166 1917 314 602 524 46 80 -255
1440 4432 1413 637 602 363 -170 17 108
];

xyz=data(:,1:3); xyz=0.0001*xyz;

% B - thermal parameter tensor. It must be transformed to beta form:
%
% exp(-(B11*h^2 + B22*k^2 + B33*l^2 + 2*B12*h*k + 2*B13*h*l + 2*B23*k*l))

Bm =0.01*data(:,4:9)/4;

Bm(:,1) = Bm(:,1)*G(1,1);
Bm(:,2) = Bm(:,2)*G(2,2);

```

```

Bm(:,3) = Bm(:,3)*G(3,3);
Bm(:,4) = Bm(:,4)*ar*br;
Bm(:,5) = Bm(:,5)*ar*cr;
Bm(:,6) = Bm(:,6)*br*cr;

```

```

atom_name = ['C(1)'; 'C(2)'; 'C(3)';
             'N(1)'; 'N(2)'; 'N(3)'; 'N(4)'; 'N(5)'; 'N(6)';
             'O(1)'; 'O(2)'; 'O(3)'; 'O(4)'; 'O(5)'; 'O(6)';
             'H(1)'; 'H(2)'; 'H(3)'; 'H(4)'; 'H(5)'; 'H(6)'] ;

```

```

*****
*****

```

```

% *** bonds.m *** Jolanta M. Snowel January 27, 1995.

```

```

% This program calculates distances between atoms.
% Calculations are performed in a non-orthogonal basis.
% g - the direct metric tensor
% G - the reciprocal metric tensor
% a, b, c, alpha, beta, gamma - unit cell parameters
% ar, br, cr Alpha, Beta, Gamma - reciprocal unit cell parameters

```

```

%atoms % *.m file. It loads data: unit cell parameters, x, y, z, and Bij (beta).

```

```

hmx_b

```

```

% g=[ a*a a*b*cos(gamma) a*c*cos(beta)
%     b*a*cos(gamma) b*b b*c*cos(alpha)
%     c*a*cos(beta) c*b*cos(alpha) c*c ]

```

```

% G = inv(g);

```

```

% BOND LENGTH (or distance between 2 atoms)

```

```

k = size(xyz); k = k(1); l=0;

```

```

for i = 1:k

```

```

    for j = (i+1):k

```

```

        v = xyz(i,:)-xyz(j,:);
        d = sqrt(v*g*v');
        if d < 1.5
            l=l+1;
            distance(l,:) = [ i j d ];

```

```

    % end
end

```


end

```
fprintf('\n \n Bond lengths in Angstroms \n \n', distance');
fprintf('%6.0f - %3.0f %12.4f\n', distance');
```

% ***** writing to a file *****

```
fid = fopen('c:\matlab\jolanta\crystal\bond.out','w');
fprintf(fid,'DATA FOR beta-HMX.\n \n ');
fprintf(fid,'\n \n Fractional coordinates in the direct lattice \n \n');
fprintf(fid,'%12.4f %12.4f %12.4f\n', xyz');
fprintf(fid,'\n \n Bond lengths in Angstroms \n \n');
fprintf(fid,'%6.0f - %3.0f \t %3.4f\n', distance');
fclose(fid)
```


```
% *** angles.m *** January 27, 1995.
% This program calculates angles between bonds.
% It requires input file such as HMX_B.M
```

% Make a table of atom numbers:

```
at = [
    5    1    6
    2    1    5
    2    1    6
    1    2    9
    2    9    3
    2    9   11
    2    9   12
    3    9   11
    3    9   12
   11    9   12
    7    4    8
    3    4    7
    3    4    8
    4    3    9
    4    3   10
    9    3   10
    3   10   14
    3   10   13
   13   10   14 ];
```

```

%   ANGLES

k = size(at); k = k(1);    ang = zeros(k,1);

for i = 1 : k

vec1 = [ at(i,2) at(i,1) ];
vec1 = xyz(vec1(1,:),) - xyz(vec1(2,:),);

vec2 = [ at(i,2) at(i,3) ];
vec2 = xyz(vec2(1,:),) - xyz(vec2(2,:),);

vec1l= sqrt(vec1*g*vec1');
vec2l= sqrt(vec2*g*vec2');

ang(i) = 57.2958*acos(vec1*g*vec2'/(vec1l*vec2l));

end

bond_angles = [at ang];

fprintf('\n \n Bond angles for beta-HMX.\n \n');

fprintf(' %12.0f  -%3.0f  -%3.0f \t %12.1f\n', bond_angles');

% *****

fid = fopen('c:\matlab\jolanta\crystal\angles.out','w');

fprintf(fid,'DATA FOR beta-HMX.\n \n ');

fprintf(fid,'\n \n Bond angles for beta-HMX.\n \n');

fprintf(fid,' %12.0f  -%3.0f  -%3.0f \t %12.1f\n', bond_angles');

fclose(fid)

*****
*****

% quadric.m                                January 27, 1995.
% This program calculates principal axes of thermal ellipsoids
% and eigenvectors. The eigenvectors are orthogonal in direct basis.

```

```

% B is a matrix of beta parameters

clear all;
hmx_b

m = size(Bm); m = m(1); j = 0; d = zeros(m,3); v = zeros(3,3*m);

for k = 1:m

B(1,1) = Bm(k,1); B(2,2) = Bm(k,2); B(3,3) = Bm(k,3);
%B(1,2) = Bm(k,4)/2; B(1,3) = Bm(k,5)/2; B(2,3) = Bm(k,6)/2;
B(1,2) = Bm(k,4); B(1,3) = Bm(k,5); B(2,3) = Bm(k,6);
B(2,1) = B(1,2); B(3,1) = B(1,3); B(3,2) = B(2,3);

Bg=(B*g);

[V,D]=eig(Bg);

d_aux=((diag(D))/(2*pi*pi)).^0.5*1000;

%d=((diag(D))/(2*pi*pi)).^0.5;

d(k,:)=d_aux';

v(1:3,j+1:j+3)=V'; j = j + 3;

end

d = d' ; d = sort(d); d = d'; clear d_aux;

fprintf('\n \n Magnitudes of the principal axes of the thermal ellipsoids. \n \n');
fprintf(' %12.1f %12.1f %12.1f \n', d');

fprintf('\n \n Eigenvectors of the thermal ellipsoids. \n \n');
fprintf(' %12.4f%12.4f%12.4f\n%12.4f%12.4f%12.4f\n%12.4f%12.4f%12.4f\n\n', v);

% ***** Writing eigenvalues and eigenvectors to QUADRIC.OUT
*****

fid = fopen('c:\matlab\jolanta\crystal\quadric.out','w');
fprintf(fid,' DATA FOR beta-HMX. \t\t\t\t\t January 27, 1995. ');
fprintf(fid,'\n \n \n \n Thermal parameters \n \n');
fprintf(fid,' %4.0f\t%4.0f\t%4.0f\t%4.0f\t%4.0f\t%4.0f\t\n', (data(:,4:9))' );
fprintf(fid,'\n \n Magnitudes of the principal axes of the thermal ellipsoids. \n \n');

```

```
fprintf(fid,'%12.1f %12.1f %12.1f \n', d');
fprintf(fid,'\f\n \n Eigenvectors of the thermal ellipsoids. \n \n');
fprintf(fid,'%12.4f%12.4f%12.4f\n%12.4f%12.4f%12.4f\n%12.4f%12.4f%12.4f\n\n',
v);
fclose(fid)
```

```
*****
*****
```

```
% *** sec_mom.m ***      Jolanta M. Snowel      June 29, 1995.
%
% This program calculates contributions to the second moment <w^2>
% from COMPLETELY EQUIVALENT NUCLEI and
% from EQUIVALENT NUCLEI with Different Directions of EFG Tensors.
% Nitrogen nuclei: spin I = 1, asymmetry parameter != zero,
% no magnetic field.

% LAST Version : sec_mom.j21, June 21, 1995.
% Two sites are considered :
%   I - N(2) in the positions: (x,y,z) & (-x,-y,-z)
%   II - N(2) in the positions: (-x,y-1/2,-z-1/2) & (x,-y+1/2,z+1/2)
%               (-x,y-1/2,z-1/2) = -(x,-y+1/2,z+1/2)

% <w^2> eqs : 2.15 & 2.16 & 2.33 S.Vega

clear all
czas = cputime;
hmx_b % hmx_b.m file. It loads data: unit cell parameters, x, y, z, and B_ij (beta).

clear Alpha Beta Gamma alpha beta gamma ar br cr a b c Bm;

t = 3; % Translation limits for n, m, and p.
atom = 2; % 1 for N(2) ; 2 for N(3)

fp = fopen('c:\matlab\jolanta\crystal\hmx_tab.out','a');
% for atom = [1 2]

fprintf(fp,'Data for HMX; \t N(%1.0f):\t translation limits t = %1.0f; \n \n',atom+1,t);
fprintf(fp,'\t cosI      cosII      <w2>(I,II) <w2>(I,I) <w2>(II,II)      <w2>-1/2
\n \n');

fprintf('Data for HMX; \t N(%1.0f):\t translation limits t = %1.0f; \n \n',atom+1,t);
fprintf('\t cosI      cosII      <w2>(I,II)      <w2>(I,I) <w2>(II,II)      <w2>-1/2 \n \n');
```

```

% ***** EFG AXES *****

% Make a table of pairs of atom numbers in each row,
% numbers refer to the sequence in 'xyz' matrix in hmx_b.m file
% (also see efg.m, efg_uc.m, & efg_ucat.m):

at = [
      6   5   1   2           % EFG for N(2)
      8   7   4   3 ];      % EFG for N(3)

at = at(atom,:);

sqrt_g = sqrt(det(g));

k = size(at,1);      efg = zeros(k*12,3); RR = zeros(k*12,3);
vector1 = zeros(4*k,3); vector2 = zeros(4*k,3); vector3 = zeros(4*k,3);

for i = 1 : k

% *****

vec1 = xyz(at(i,2),:) - xyz(at(i,1),:);      % [EFG]1 = [O - O] <--- auxiliary
vec2 = xyz(at(i,4),:) - xyz(at(i,3),:);      % [EFG]2 = [N - N]

vec1l= sqrt(vec1*g*vec1');
vec2l= sqrt(vec2*g*vec2');

vec1 = vec1/vec1l;
vec2 = vec2/vec2l;

vector2(i,:) = vec2;

% ***** [EFG]3 = [O - O] x [N - N] *****

vec3(1) = sqrt_g*( vec1(2)*vec2(3) - vec1(3)*vec2(2) );
vec3(2) = sqrt_g*( vec1(3)*vec2(1) - vec1(1)*vec2(3) );
vec3(3) = sqrt_g*( vec1(1)*vec2(2) - vec1(2)*vec2(1) );

vector3l = sqrt(vec3*g*vec3');
vector3(i,:) = (vec3/vector3l)*G ;
vec3 = vec3*g ;

% ***** [EFG]1 = [EFG]2 x [EFG]3 *****

```

```

vector1(i,1) = sqrt_g*( vec2(2)*vec3(3) - vec2(3)*vec3(2) ) ;
vector1(i,2) = sqrt_g*( vec2(3)*vec3(1) - vec2(1)*vec3(3) ) ;
vector1(i,3) = sqrt_g*( vec2(1)*vec3(2) - vec2(2)*vec3(1) ) ;

vector1(i,:) = vector1(i,:)*G ;
vector1l = sqrt(vector1(i,:)*g*vector1(i,:));
vector1(i,:) = vector1(i,:)/vector1l;

end % ***** END *****

% ***** EFG axes of all N(2) and N(3) in equivalent positions *****

vector1(k+1:2*k,:) = [-vector1(1:k,1) vector1(1:k,2) -vector1(1:k,3)]; % 2)
-x,y+1/2,-z+1/2
vector2(k+1:2*k,:) = [-vector2(1:k,1) vector2(1:k,2) -vector2(1:k,3)]; % + 0.5
;
vector3(k+1:2*k,:) = [-vector3(1:k,1) vector3(1:k,2) -vector3(1:k,3)]; % + 0.5
;

vector1(2*k+1:3*k,:) = -vector1(1:k,:) ; % (3) -x,-y,-z
vector2(2*k+1:3*k,:) = -vector2(1:k,:) ;
vector3(2*k+1:3*k,:) = -vector3(1:k,:) ;

vector1(3*k+1:4*k,:) = -vector1(k+1:2*k,:); % (4) x,-y+1/2,z+1/2
vector2(3*k+1:4*k,:) = -vector2(k+1:2*k,:); % + 0.5 ;
vector3(3*k+1:4*k,:) = -vector3(k+1:2*k,:); % + 0.5 ;

% *****

E = [vector1(1,:) ; vector2(1,:) ; vector3(1,:)] ; invE = inv(E) ;
% E = [vector1(3,:) ; vector2(3,:) ; vector3(3,:)] ; invE = inv(E) ;

n=1; l=3;

for i = 1 : 4*k

efg(n:l,:) = [vector1(i,:) ; vector2(i,:) ; vector3(i,:)];

F = efg(n:l,:);

RR(n:l,:) = E*inv(F);

n = 1 + 1; l = 1 + 3;

```

end

% ***** END OF CALCULATIONS OF THE EFG TENSORS

% ***** & TRANSFORMATION MATRIX [RR]

%

% ***** POSITIONS OF EQUIVALENT NUCLEI { N(2) }

% Either atoms N(2) or N(3) from 'xyz' matrix (hmx_b.m file) are considered:

m = 1 ;
xyz_d = zeros(m*4,3);
xyz_d(1,:) = xyz(atom+1,:); % fractional coordinates of N(2) or N(3)

% *** xyz_d - matrix of the coordinates of nitrogen N(2) atoms
% *** in the following positions:
% *** (1) x,y,z (2) -x,y-1/2,-z-1/2 (3) -x,-y,-z (4) x,-y+1/2,z+1/2 .
% *** (1) & (3) - 1st molecule; (2) & (4) - 2nd & 3rd molecule;

xyz_d(m+1:2*m,1) = -xyz_d(1:m,1) ; % 2) -x,y-1/2,-z-1/2
xyz_d(m+1:2*m,2) = xyz_d(1:m,2) + 0.5 ;
xyz_d(m+1:2*m,3) = -xyz_d(1:m,3) + 0.5 ;

%xyz_d(m+1:2*m,1) = -xyz_d(1:m,1) ; % 2) -x,y+1/2,-z+1/2
%xyz_d(m+1:2*m,2) = xyz_d(1:m,2) - 0.5 ;
%xyz_d(m+1:2*m,3) = -xyz_d(1:m,3) - 0.5 ;

xyz_d(2*m+1:3*m,1) = -xyz_d(1:m,1) ; % (3) -x,-y,-z
xyz_d(2*m+1:3*m,2) = -xyz_d(1:m,2) ;
xyz_d(2*m+1:3*m,3) = -xyz_d(1:m,3) ;

xyz_d(3*m+1:4*m,1) = xyz_d(1:m,1) ; % (4) x,-y+1/2,z+1/2
xyz_d(3*m+1:4*m,2) = -xyz_d(1:m,2) + 0.5 ;
xyz_d(3*m+1:4*m,3) = xyz_d(1:m,3) + 0.5 ;

```

% ***** cosines *****

k = size(efg,1);    count1 = 0; count2 = 0;

i=1;
for j=1:(k/3)
    vic2(j,:) = efg(i,:)*invE;
    i=i+3;
end

% *****
%Omega = zeros(216,4); ANG1 = zeros(216,1); ANG2 = zeros(216,1); DA =
zeros(216,1);
%CosI =zeros(216,1); CosII =zeros(216,1);
% *****

count2 = 0;    count3 = 0;

%c1=6; c2=2; c3=3; [-5 -3 -1 1 4 11] ; [-3 -1 5]

%for c1 = [-11 -2 4 ]
%for c2 = [-4 -1 3]
%for c3 = [-3 0 5]

for c1 =4
for c2 =3
for c3 =0

vic1 = [c1 c2 c3]/(sqrt([c1 c2 c3]*[c1 c2 c3]'));

for i = 1:4
    cos_table(i) = [vic1*vic2(i,:)'];
end

count1=count1+1;
cosinus_table(count1,:) = cos_table;

% ***** SECOND MOMENT CONTRIBUTION FROM EQUIVALENT NUCLEI
*****
% ***** WITH DIFFERENT DIRECTIONS OF THE EFG TENSORS
*****

SecMoment = zeros(6,1);    SecMom = 0;    %SecondMom = 0;
Da = 0;    Ang1 = 0; Ang2 = 0;

```



```
% ***** Distance between 2 atoms *****
```

```
k = size(xyz_d,1); l=0;
```

```
for i = 1:4
```

```
    cosI = cos_table(i);
```

```
    v1 = xyz_d(i,:);
```

```
for h = 0:1
```

```
    h = i + 2*h;
```

```
    j = rem(h,4) + 1;
```

```
    cosII=cos_table(j);
```

```
    R = RR(3*j-2:3*j,:); % *** Transformation matrix ****
```

```
    v2 = xyz_d(j,:);
```

```
for m = -t:t
```

```
    v2(1) = xyz_d(j,1) + m ;
```

```
for n = -t:t
```

```
    v2(2) = xyz_d(j,2) + n ;
```

```
for p = -t:t
```

```
    v2(3) = xyz_d(j,3) + p ;
```

```
    v = v2 - v1 ;
```

```
    r = sqrt(v*g*v') ;
```

```
    l=l+1;
```

```
    D = v*invE ;
```

```
%    d_o = sqrt(D*D') ;
```

```
X = D(1)/r; Y = D(2)/r; Z = D(3)/r;
```

```
XOS = 1 - 3*D(1)*D(1)/(r*r);
```

```
YOS = 1 - 3*D(2)*D(2)/(r*r);
```

```
ZOS = 1 - 3*D(3)*D(3)/(r*r);
```

```
count2 = count2 + 1;
```

```
% *** Dipolar Hamiltonian ***
```

```
% h1 = h_23 = h_32; h2 = h_56 = h_65; h3 = h_78 = h_87;
```

```
h1 = R(3,3)*ZOS - 3*R(2,3)*Y*Z - 3*R(1,3)*X*Z ;
```

```
h2 = R(1,1)*XOS - 3*R(2,1)*X*Y - 3*R(3,1)*X*Z ;
```

```

h3 = R(2,2)*YOS - 3*R(1,2)*X*Y - 3*R(3,2)*Y*Z ;

% *** SECOND MOMENT for Equivalent Nuclei with Different Directions of the EFG
Tensors. ****
% *** eq. 2.33 ***

ang1 = cosI*cosII/(cosI*cosI + cosII*cosII);

dipol = 2*h1*h1 + 2*h3*h3 + 4*h2*h2 - 8*h1*h3*ang1;

SM = dipol/(r*r*r*r*r*r);

%SM = ( 2*h1*h1 + 2*h3*h3 + 4*h2*h2 - 8*h1*h3*cosI*cosII/(cosI*cosI +
cosII*cosII))/r^6;

SecMom = SecMom + SM ; % Da = Da + da; Ang1 = Ang1 +
ang1;

% Distance(l,:) = [ i j m n p r SM ] ;

% ang1 = 0;

end % end of ' for p = -t:t '
end % end of ' for n = -t:t '
end % end of ' for m = -t:t '
end % end of ' for h = 0:1 '
SecMoment(i) = SecMom;
SecMom = 0 ;
SM = 0;
end % end of ' for i = 1:4 '

% DA(count1) = Da/8; Da = 0;
% ANG1(count1) = Ang1/8;

SecMoment = SecMoment*2592200; % const = (1/6)*gamma^4*h_bar^2

%fprintf('\n \n Distance between 2 atoms in Angstroms and Second Moments \n \n');
%fprintf('\n \n Equivalent nuclei with different directions of EFG tensors\n \n');
%fprintf('%6.0f - %3.0ft %3.0f %3.0f %3.0f %12.4f%24.8f \n',Distance');

%fprintf(fp,'\n \n Distance between 2 atoms in Angstroms and Second Moments \n \n');
%fprintf(fp,'\n \n Equivalent nuclei with different directions of EFG tensors\n \n');
%fprintf(fp,'%6.0f - %3.0ft %3.0f %3.0f %3.0f %12.4f%24.8f \n',Distance');

```

```
% ***** SECOND MOMENT CONTRIBUTION FROM COMPLETELY EQUIVALENT
NUCLEI *****
```

```
SecMom = 0;
```

```
% ***** Distance between 2 atoms *****
```

```
k = size(xyz_d,1); l=0; % Distance = zeros((k*k-k)/2,4);
```

```
cosI = cos_table(1); cosII = cos_table(2);
```

```
for i = 1:2
```

```
    v1 = xyz_d(i,:);
```

```
for j = i+1:k
```

```
    vle = xyz_d(j,:);
```

```
for m = -t:t
```

```
    vle(1) = xyz_d(j,1) + m;
```

```
for n = -t:t
```

```
    vle(2) = xyz_d(j,2) + n;
```

```
for p = -t:t
```

```
    vle(3) = xyz_d(j,3) + p;
```

```
    v = vle - v1 ;
```

```
    r = sqrt(v'*v) ;
```

```
    if r > 0.1
```

```
        l=l+1;
```

```
        D = v*invE ;
```

```
        % d_o = sqrt(D*D') ;
```

```
    X = D(1)/r; Y = D(2)/r; Z = D(3)/r;
```

```
    XOS = 1 - 3*D(1)*D(1)/(r*r);
```

```
    YOS = 1 - 3*D(2)*D(2)/(r*r);
```

```
    ZOS = 1 - 3*D(3)*D(3)/(r*r);
```

```
count3 = count3 + 1;
```

```
% <w^2> = sum( 8*XOS^2 + 4*YOS^2 + 4*ZOS^2 - 8*YOS*ZOS)/r^6 %
completely equivalent nuclei
```

```
% *** SECOND MOMENT for Completely Equivalent Nuclei. *****
```

```
% *** eq. 2.15 ***
```

```
SM = (8*XOS*XOS + 4*YOS*YOS + 4*ZOS*ZOS - 8*YOS*ZOS)/(r*r*r*r*r*r);
```

```
SecMom = SecMom + SM ;
```

```
% *** Dipolar Hamiltonian ***
```

```
% Distance(l,:) = [ i j m n p r SM ] ;
```

```
end % end of ' if r>0.1 '
```

```
end % end of ' for p = -t:t '
```

```
end % end of ' for n = -t:t '
```

```
end % end of ' for m = -t:t '
```

```
end % end of ' for j = i:2:i+2 '
```

```
ang2 = cosI*cosI/(cosI*cosI + cosII*cosII);
```

```
SecMoment(i+4) = 1296100*SecMom*ang2; % const =  
(1/12)*gamma^4*h_bar^2
```

```
SecMom = 0 ;
```

```
%fprintf(' \n Distance between 2 atoms in Angstroms and Second Moments \n \n');
```

```
%fprintf(' \n Equivalent nuclei\n \n');
```

```
%fprintf('%6.0f - %3.0ft %3.0f %3.0f %3.0f %12.4f%24.8f \n',Distance');
```

```
%fprintf(fp,' Distance between 2 atoms in Angstroms and Second Moments \n \n');
```

```
%fprintf(fp,'\n Equivalent nuclei\n \n');
```

```
%fprintf(fp,'%6.0f - %3.0ft %3.0f %3.0f %3.0f %12.4f%24.8f \n',Distance');
```

```
end % end of ' for i = 1:2 '
```

```
Omega_2(1) = (sum(SecMoment(1:4)))/4;
```

```
Omega_2(2) = SecMoment(5)/2;
```

```
Omega_2(3) = SecMoment(6)/2;
```

```
Omega_2(4) = sqrt((sum(SecMoment(1:4)))/4+0.5*SecMoment(5)+0.5*SecMoment(6));
```

```
Omega(count1,:) = Omega_2;
```

```
SecondMom(count1,:) = SecMoment';
```

```
omega_2(1) = (sum(SecondMom(1:4)))/4;
```

```
omega_2(2) = SecondMom(5)/2;
```

```
omega_2(3) = SecondMom(6)/2;
```

```
omega_2(4) =
```

```
sqrt((sum(SecondMom(1:4)))/4+0.5*SecondMom(5)+0.5*SecondMom(6));
```

```
omega_2m = mean(Omega);
```

```

fprintf(fp,'\t %10.3f %10.3f    %12.0f%12.0f%12.0f %14.0f
\n',cosI,cosII,Omega(count1,:));
fprintf('\t %10.3f %10.3f    %12.0f%12.0f%12.0f %14.0f
\n',cosI,cosII,Omega(count1,:));

end % end of ' for c3 = '
end % end of ' for c2 = '
end % end of ' for c1 = '

fprintf(fp,'\n\n');
fprintf('\n\n');

%fprintf('%8.3f\t%8.3f\t%10.0f\t%10.0f\t%10.0f\t%10.0f \n',[cosinus_table(:,1:2)
Omega]);
%fprintf(fp,'\n\n%8.3f\t%8.3f\t%10.0f\t%10.0f\t%10.0f\t%10.0f
\n',cosI,cosII,omega_2);

% end      % end of ' for atom = [1 2] '
fclose(fp);

Czas = cputime - czas;
%Cz = fix(clock);

*****
*****

% *** hmx_2o.m ***      Jolanta M. Snowel      July 19, 1995.
%
% This program calculates second order contributions to the second moment <w^2>
% from Unlike Spins.
% Nitrogen nuclei: spin I = 1, asymmetry parameter != zero,
% no magnetic field.

% LAST Version : sec_mom.j21, June 21, 1995.
% Two sites are considered :
% I - N(2) in the positions: (x,y,z) & (-x,-y,-z)
% II - N(2) in the positions: (-x,y-1/2,-z-1/2) & (x,-y+1/2,z+1/2)
% (-x,y-1/2,z-1/2) = -(x,-y+1/2,z+1/2)

% <w^2> eqs : 2.16 & 3.27 S.Vega

clear all
czas = cputime;

```

```

hmx_b    % hmx_b.m file. It loads data: unit cell parameters, x, y, z, and B_ij (beta).
t = 3;    % Translation limits for n, m, and p.
atom = 1; % 1 for N(2) ; 2 for N(3)

fp = fopen('c:\jolanta\hmx\hmx_2o.dat','w');
%for atom = [1 2]
count2 = 0;

% ***** EFG AXES *****

% Make a table of pairs of atom numbers in each row,
% numbers refer to the sequence in 'xyz' matrix in hmx_b.m file
% (also see efg.m, efg_uc.m, & efg_ucat.m):

at = [
      6   5   1   2      % EFG for N(2)
      8   7   4   3 ];  % EFG for N(3)

at = at(atom,:);

sqrt_g = sqrt(det(g));

k = size(at,1);    efg = zeros(k*12,3); RR = zeros(k*12,3);
vector1 = zeros(4*k,3); vector2 = zeros(4*k,3); vector3 = zeros(4*k,3);

for i = 1 : k

% *****

vec1 = xyz(at(i,2),:) - xyz(at(i,1),:);    % [EFG]1 = [O - O] <--- auxiliary
vec2 = xyz(at(i,4),:) - xyz(at(i,3),:);    % [EFG]2 = [N - N]

vec1l= sqrt(vec1*g*vec1');
vec2l= sqrt(vec2*g*vec2');

vec1 = vec1/vec1l;
vec2 = vec2/vec2l;

vector2(i,:) = vec2;

% ***** [EFG]3 = [O - O] x [N - N] *****

vec3(1) = sqrt_g*( vec1(2)*vec2(3) - vec1(3)*vec2(2) );
vec3(2) = sqrt_g*( vec1(3)*vec2(1) - vec1(1)*vec2(3) );

```

```

vec3(3) = sqrt_g*( vec1(1)*vec2(2) - vec1(2)*vec2(1) ) ;

vector3l = sqrt(vec3*G*vec3');
vector3(i,:) = (vec3/vector3l)*G ;
vec3 = vec3*G ;

% ***** [EFG]1 = [EFG]2 x [EFG]3 *****

vector1(i,1) = sqrt_g*( vec2(2)*vec3(3) - vec2(3)*vec3(2) ) ;
vector1(i,2) = sqrt_g*( vec2(3)*vec3(1) - vec2(1)*vec3(3) ) ;
vector1(i,3) = sqrt_g*( vec2(1)*vec3(2) - vec2(2)*vec3(1) ) ;

vector1(i,:) = vector1(i,:)*G ;
vector1l = sqrt(vector1(i,:)*g*vector1(i,:));
vector1(i,:) = vector1(i,:)/vector1l;

end % ***** END *****

% ***** EFG axes of all N(2) and N(3) in equivalent positions *****

vector1(k+1:2*k,:) = [-vector1(1:k,1) vector1(1:k,2) -vector1(1:k,3)]; % 2)
-x,y+1/2,-z+1/2
vector2(k+1:2*k,:) = [-vector2(1:k,1) vector2(1:k,2) -vector2(1:k,3)]; % + 0.5
;
vector3(k+1:2*k,:) = [-vector3(1:k,1) vector3(1:k,2) -vector3(1:k,3)]; % + 0.5
;

vector1(2*k+1:3*k,:) = -vector1(1:k,:) ; % (3) -x,-y,-z
vector2(2*k+1:3*k,:) = -vector2(1:k,:) ;
vector3(2*k+1:3*k,:) = -vector3(1:k,:) ;

vector1(3*k+1:4*k,:) = -vector1(k+1:2*k,:); % (4) x,-y+1/2,z+1/2
vector2(3*k+1:4*k,:) = -vector2(k+1:2*k,:); % + 0.5 ;
vector3(3*k+1:4*k,:) = -vector3(k+1:2*k,:); % + 0.5 ;

% *****

E = [vector1(1,:) ; vector2(1,:) ; vector3(1,:)]; invE = inv(E) ; % EFG_x
% E = [vector1(3,:) ; vector2(3,:) ; vector3(3,:)]; invE = inv(E) ;

n=1; l=3;

for i = 1 : 4*k

```

```

efg(n:1,:) = [vector1(i,:) ; vector2(i,:) ; vector3(i,:)];

F = efg(n:1,:);

RR(n:1,:) = E*inv(F);

n = 1 + 1;    l = 1 + 3;

end

% ***** END OF CALCULATIONS OF THE EFG TENSORS
%*****

% ***** & TRANSFORMATION MATRIX [RR]
%*****

%
%*****

%*****

% ***** POSITIONS OF EQUIVALENT NUCLEI { N(2) }
%*****

% Either atoms N(2) or N(3) from 'xyz' matrix (hmx_b.m file) are considered:

m = 5 ;
xyz_d = zeros(m*4,3);
xyz_d(1,:) = xyz(atom+1,:);    % fractional coordinates of N(2) or N(3)
xyz_d(2:5,:) = xyz(11:14,:);   % fractional coordinates of protons

% ***   xyz_d - matrix of the coordinates of nitrogen N(2) atoms
% ***   in the following positions:
% ***   (1) x,y,z  (2) -x,y-1/2,-z-1/2  (3) -x,-y,-z  (4) x,-y+1/2,z+1/2 .
% ***   (1) & (3) - 1st molecule;    (2) & (4) - 2nd & 3rd molecule;

xyz_d(m+1:2*m,1) = -xyz_d(1:m,1)    ;    % 2) -x,y-1/2,-z-1/2
xyz_d(m+1:2*m,2) = xyz_d(1:m,2) + 0.5    ;
xyz_d(m+1:2*m,3) = -xyz_d(1:m,3) + 0.5    ;

%xyz_d(m+1:2*m,1) = -xyz_d(1:m,1)    ;    % 2) -x,y+1/2,-z+1/2
%xyz_d(m+1:2*m,2) = xyz_d(1:m,2) - 0.5    ;

```



```

%xyz_d(m+1:2*m,3) = -xyz_d(1:m,3) - 0.5 ;

xyz_d(2*m+1:3*m,1) = -xyz_d(1:m,1) ; % (3) -x,-y,-z
xyz_d(2*m+1:3*m,2) = -xyz_d(1:m,2) ;
xyz_d(2*m+1:3*m,3) = -xyz_d(1:m,3) ;

xyz_d(3*m+1:4*m,1) = xyz_d(1:m,1) ; % (4) x,-y+1/2,z+1/2
xyz_d(3*m+1:4*m,2) = -xyz_d(1:m,2) + 0.5 ;
xyz_d(3*m+1:4*m,3) = xyz_d(1:m,3) + 0.5 ;

% ***** * *****

k = size(efg,1); count1 = 0; count2 = 0;

i=1;
for j=1:(k/3)
    vic2(j,:) = efg(i,:)*invE;
    i=i+3;
end

%*****

% ***** SECOND MOMENT CONTRIBUTION FROM UNLIKE SPINS *****

SecMoment = zeros(6,1); SecMom = 0; %SecondMom = 0;

% ***** Distance between 2 atoms *****

k = size(xyz_d,1); count1 = 0 ;

% vi spin I (nitrogen) % vs (hydrogen) % vt (hydrogen)

%for i = 1:5:20
for i = [1 6]

    sm_NH = 0 ;
    vi = xyz_d(i,:);

    for j = [2:5 7:10 12:15 17:20]
        for l = [2:5 7:10 12:15 17:20]

```

```

if (l > j)

%      vs = xyz_d(j,:);
%      vt = xyz_d(l,:);

for ms = -t:t
    vs(1) = xyz_d(j,1) + ms ;
for ns = -t:t
    vs(2) = xyz_d(j,2) + ns ;
for ps = -t:t
    vs(3) = xyz_d(j,3) + ps ;

for mt = -t:t
    vt(1) = xyz_d(l,1) + ms ;
for nt = -t:t
    vt(2) = xyz_d(l,2) + ns ;
for pt = -t:t
    vt(3) = xyz_d(l,3) + ps ;

countl = countl + 1 ;

v_s = vs - vi ;
v_t = vt - vi ;
r_s = sqrt(v_s*g*v_s') ;
r_t = sqrt(v_t*g*v_t') ;

D_s = v_s*invE ;

X_s(1) = D_s(1)/r_s;    Y_s(1) = D_s(2)/r_s;    Z_s(1) = D_s(3)/r_s;

XOS_s(1) = 1 - 3*D_s(1)*D_s(1)/(r_s*r_s);
YOS_s(1) = 1 - 3*D_s(2)*D_s(2)/(r_s*r_s);
ZOS_s(1) = 1 - 3*D_s(3)*D_s(3)/(r_s*r_s);

D_t = v_t*invE ;

X_t(1) = D_t(1)/r_t;    Y_t(1) = D_t(2)/r_t;    Z_t(1) = D_t(3)/r_t;

XOS_t(1) = 1 - 3*D_t(1)*D_t(1)/(r_t*r_t);
YOS_t(1) = 1 - 3*D_t(2)*D_t(2)/(r_t*r_t);
ZOS_t(1) = 1 - 3*D_t(3)*D_t(3)/(r_t*r_t);

```

```

% *** Second Order Contributions from Unlike Spins. ****
% *** eq. 3.27 ***

sm = (2*ZOS_s*ZOS_s*ZOS_t*ZOS_t + ...
      9*(ZOS_s*ZOS_s*(X_t*X_t + Y_t*Y_t) + ZOS_t*ZOS_t*(X_s*X_s +
Y_s*Y_s)) + ...
      81*(X_s*X_s*X_t*X_t + Y_s*Y_s*Y_t*Y_t + ...
      X_s*X_s*Y_t*Y_t + Y_s*Y_s*X_t*X_t) )/r_s^6/r_t^6 ;

sm_NH = sm_NH + sm ;

% Distance(count1,:) = [i j l r_s r_t sm] ;

fprintf(fp,'%6.0f -%3.0f -%3.0f\t %8.4f %10.4f %22.10f \n',[i j l r_s r_t sm]);

end % end ' for pt = -t:t '
end % end ' for nt = -t:t '
end % end ' for mt = -t:t '
end % end ' for ps = -t:t '
end % end ' for ns = -t:t '
end % end ' for ms = -t:t '

end % end ' if (l > j) '

end % end ' for l = [2:5 7:10 12:15 17:20] '
end % end ' for j = [2:5 7:10 12:15 17:20] '

count2 = count2 + 1;
SM_NH(count2) = sm_NH;

end % end ' for i = 1:5:20 '

% const = (1.9338*26.7520*1.05459)^4/(16*pi*pi*1564*1564)*1000000 ;
% N(3)
const = (1.9338*26.7520*1.05459)^4/(16*pi*pi*1441*1441)*1000000 ;
% N(2)

SM_NH_av = 0.5*sum(SM_NH*const); % const =
(1/4)*gamma_N^4*gamma_H^4*h_bar^6/(E_x -E_y)^2

fprintf('%6.0f - %3.0f\t %3.0f %3.0f %3.0f %12.4f%12.4f%12.4f%20.8f
\n',Distance');

```

```
% ***** writing to a file *****
fprintf(fp,'Data for HMX ; N(%1.0f)\t t = %1.0f;\t count1 = %12.0f \t Dell
\n',atom+1,t,count1);
fprintf(fp,'\n\n SM_NH =\t%20.6f %20.6f %20.6f %20.6f \n', SM_NH);
fprintf(fp,'\n\n SM_NH_av =%20.6f sqrt(SM_NH_av) = %20.6f \n\n \n', [SM_NH_av
sqrt(SM_NH_av)]);
%end
fclose(fp);
```

```
SM_NH'
SM_NH_av
```

```
Czas = cputime - czas
%Cz = fix(clock);
%save last_s.mat
```

```
*****
*****
```